

DESCRIPTION

Phosphor and Phosphor Paste

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Technical field

The present invention relates to a phosphor and a phosphor paste.

Background art

Phosphors are used in fluorescent lamps, luminous indications,
10 X-ray inspection systems, CRTs, vacuum ultraviolet excited
light-emitting devices and so on. Known phosphors include aluminates
[for example, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$] and borates [for example, $(\text{Y,Gd})\text{BO}_3:\text{Eu}$]
as red phosphors, silicates [for example, $\text{CaMgSi}_2\text{O}_6:\text{Eu}$] as blue phosphors
and silicates [for example, $\text{Zn}_2\text{SiO}_4:\text{Mn}$] as green phosphors, and they
15 are used in plasma displays (hereinafter, referred to as PDPs) and
vacuum ultraviolet excited light-emitting devices such as rare gas
lamps.

The vacuum ultraviolet excited light-emitting devices are
light-emitting devices in which plasma is generated by electric
20 discharge in a rare gas, and a phosphor is excited by irradiating vacuum
ultraviolet rays emitted from the plasma onto the phosphor, thereby
resulting in emitting visible rays from the phosphor.

The brightness of the conventional phosphors decreases when the
phosphor is exposed to the plasma.

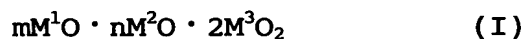
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Disclosure of the invention

An object of the present invention is to provide a phosphor having a high brightness even when it is exposed to plasma, and to provide a phosphor paste comprising the phosphor.

5 As the result of extensive researches for solving the above problems under these circumstances, the present inventors have found a phosphor with a high brightness by combining a specific silicate and aluminate and thus they has completed the present invention.

Therefore, the present invention provides a phosphor comprising
10 a fluorescent substance A¹ containing a compound represented by the following formula (I) and at least one activator selected from the group consisting of Eu and Mn, and a fluorescent substance B¹ containing an aluminate;



15 [in the formula (I),

M¹ is at least two selected from the group consisting of Ca, Sr and Ba, or Ca alone or Ba alone;

M² is at least one selected from the group consisting of Mg and Zn;

20 M³ is at least one selected from the group consisting of Si and Ge;

$$0.5 \leq m \leq 3.5; \text{ and}$$

$$0.5 \leq n \leq 2.5].$$

Further, the present invention provides a phosphor paste
25 comprising the phosphor, a solvent and a binder.

The phosphor of the present invention has a high brightness after being exposed to plasma, and is suitable for vacuum ultraviolet excited light-emitting devices such as PDP and rare gas lamp. The phosphor and the phosphor paste provide a vacuum ultraviolet excited light-emitting device with a high brightness and a long life.

Mode for carrying out the invention

The phosphor of the present invention includes a fluorescent substance A¹. The fluorescent substance A¹ contains a compound represented by the above formula (I) and at least one selected from the group consisting of Eu and Mn as an activator.

In the formula (I),

M¹ is at least two selected from the group consisting of Ca, Sr and Ba, or Ca alone or Ba alone;

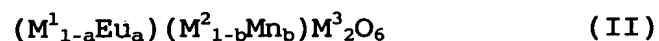
M² is at least one selected from the group consisting of Mg and Zn;

M³ is at least one selected from the group consisting of Si and Ge;

$0.5 \leq m \leq 3.5$; and

$0.5 \leq n \leq 2.5$.

It is preferable that the fluorescent substance A¹ is a compound represented by the following formula (II):



[in the formula (II),

M¹ is at least two selected from the group consisting of Ca,

Sr and Ba, or Ca alone or Ba alone;

M^2 is at least one selected from the group consisting of Mg and Zn;

M^3 is at least one selected from the group consisting of Si and

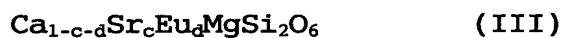
5 Ge;

$$0 \leq a \leq 0.5;$$

$$0 \leq b \leq 0.5; \text{ and}$$

$$0 < a + b].$$

It is more preferable that the fluorescent substance A^1 is a
10 compound represented by the following formula (III):



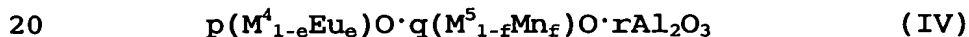
[in the formula (III),

$$0 \leq c \leq 0.1; \text{ and}$$

$$0 < d \leq 0.1].$$

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The phosphor of the present invention includes a fluorescent substance B^1 other than the fluorescent substance A^1 . The fluorescent substance B^1 is an aluminate and preferably a compound represented by the following formula (IV):



[in the formula (IV),

M^4 is at least one selected from the group consisting of Ca, Sr and Ba;

M^5 is at least one selected from the group consisting of Mg and

25 Zn;

$$0.5 \leq p \leq 1.5;$$

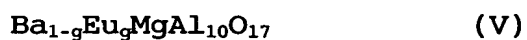
$$0.5 \leq q \leq 1.5;$$

$$4.5 \leq r \leq 5.5;$$

$$0 < e \leq 0.5; \text{ and}$$

$$5 \quad 0 < f \leq 0.1].$$

It is preferable that the fluorescent substance B^1 is a compound represented by the following formula (V):



[in the formula (V),

$$10 \quad 0 < g \leq 0.3].$$

The weight ratio of fluorescent substance A^1 /fluorescent substance B^1 is preferably from 5/95 to 95/5, more preferably from 20/80 to 90/10, and further preferably from 30/70 to 85/15. When the weight ratio of fluorescent substance A^1 /fluorescent substance B^1 is within the above range, the obtained phosphor has a higher brightness when it is exposed to plasma.

When the both of the fluorescent substance A^1 and the fluorescent substance B^1 are in form of particles, the fluorescent substance A^1 has a primary particle diameter of usually $0.1 \mu\text{m}$ to $5 \mu\text{m}$, preferably $0.3 \mu\text{m}$ to $3 \mu\text{m}$. The fluorescent substance B^1 has a primary particle diameter of usually $0.1 \mu\text{m}$ to $5 \mu\text{m}$, preferably $0.3 \mu\text{m}$ to $3 \mu\text{m}$. It is preferable that D_B^1 , the average primary particle diameter of the fluorescent substance B^1 , is 0.2-5 times D_A^1 , the primary particle diameter of the fluorescent substance A^1 , namely, $D_A^1/D_B^1 \leq 5$ and D_B^1/D_A^1

≤ 5 are satisfied.

The phosphor of the present invention may include other phosphor insofar as it includes the fluorescent substance A¹ and the fluorescent substance B¹.

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The phosphor of the present invention is excited by vacuum ultraviolet rays and has a high brightness, even when it is exposed to plasma. In the production of PDP and rare gas lamp, a phosphor layer is formed usually by a production method including steps of
10 mixing a phosphor, a binder and a solvent to obtain a phosphor paste, coating the phosphor paste on a light-emitting unit, and heat-treating the light-emitting unit (for example, at 500°C). The phosphor of the present invention has a brightness comparable to that before the heat treatment even after being subjected to the heat treatment
15 as described above. Accordingly, when the phosphor of the present invention is used in vacuum ultraviolet excited light-emitting devices such as PDP and a rare gas lamp, PDP and a rare gas lamp with a high brightness and long life can be obtained.

In addition, the phosphor of the present invention is also excited
20 by ultraviolet rays, X-rays, electron beams other than vacuum ultraviolet rays. The phosphor may be used in fluorescent lamps, luminous indications, X-ray inspection systems, CRTs and so on.

The phosphor with a high brightness according to the present
25 invention may be produced, for example, by a method of mixing the

fluorescent substance A^1 with the fluorescent substance B^1 . The mixing may be carried out using an apparatus such as stirrer, ball mill and triplerollermill. In the mixing, a phosphor other than the fluorescent substance A^1 and the fluorescent substance B^1 may be added, if necessary.

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The fluorescent substance A^1 may be prepared, for example, by calcining a mixture of metal compounds which is converted to the fluorescent substance A^1 by calcination.

Examples of calcium source, strontium source, barium source
10 (corresponding to M^1 in the formula (I)) in the mixture include a compound which is decomposed to be an oxide at high temperature such as hydroxide, carbonate, nitrate, halide and oxalate having a purity of not less than 99%, or an oxide having a purity of not less than 99.9%.

Examples of magnesium source, zinc source (corresponding to M^2
15 in the formula (I)) in the mixture include a compound which is decomposed to be an oxide at high temperature such as hydroxide, carbonate, nitrate, halide and oxalate having a purity of not less than 99%, or an oxide having a purity of not less than 99%.

Examples of silicon source, germanium source (corresponding to
20 M^3 in the formula (I)) in the mixture include a compound which is decomposed to be an oxide at high temperature such as hydroxide, carbonate, nitrate, halide and oxalate having a purity of not less than 99%, or an oxide having a purity of not less than 99%.

Examples of europium source, manganese source (an activator for
25 the fluorescent substance A^1) in the mixture include a compound which

is decomposed to be an oxide at high temperature such as hydroxide, carbonate, nitrate, halide and oxalate having a purity of not less than 99%, or an oxide having a purity of not less than 99%.

The fluorescent substance A¹ is prepared by mixing the above
5 compounds weighed such that predetermined composition of fluorescent substance A¹ is obtained and calcining the mixture.

The mixing may be carried out, for example, using a ball mill, V-type mixer or stirrer. In the mixing, an appropriate amount of a flux may be added. By addition of a flux, the formation of the phosphor
10 is promoted and calcination at a lower temperature becomes possible.

The calcination is preferably carried out under a reductive atmosphere, for example, under nitrogen atmosphere containing about 0.1% by volume to about 10% by volume of hydrogen, or argon atmosphere containing about 0.1% by volume to about 10% by volume of hydrogen.
15 Usually, the calcination may be carried out under conditions of temperature of from about 1,000°C to about 1,500°C and time of from about 1 hour to about 100 hours.

When the mixture contains a compound which is decomposed to be an oxide at high temperature such as hydroxide, carbonate, nitrate,
20 halide and oxalate, the mixture may be pre-calcined before the calcination.

The pre-calcination may be carried out under any of oxidative atmosphere (for example, under air) and reductive atmosphere. The pre-calcination may usually be conducted at temperature of from about
25 600°C to about 900°C.

The fluorescent substance A¹ may be pulverized, washed or classified, if necessary. The pulverization may be carried out, for example, using a ball mill or jet mill. The pulverized fluorescent substance A¹ may be heat-treated. Crystallinity of the fluorescent substance A¹ (which is lowered by pulverization) may be enhanced by the heat treatment. The heat treatment may usually be carried out under the same conditions as those for the calcination described above.

Further, the fluorescent substance A¹ used in the present invention may be prepared, for example, by a method described in JP-A-2002-332481 or JP-A-2003-183644.

The fluorescent substance B¹ may be prepared, for example, by calcining a mixture of metal compounds which is converted to the fluorescent substance B¹ by calcination.

When the fluorescent substance B¹ contains, for example, barium (Ba), europium (Eu), magnesium (Mg), aluminum (Al) and oxygen (O):

Examples of barium source, europium source, magnesium source, and aluminum source in the mixture include a compound which is decomposed to be an oxide at high temperature and an oxide having a purity of not less than 99.9%.

The fluorescent substance B¹ is prepared by mixing the above compounds weighed such that predetermined composition of fluorescent substance B¹ is obtained and calcining the mixture.

The mixing, calcination and optional pre-calcination may be carried out under the same conditions as those for the fluorescent

substance A¹. The fluorescent substance B¹ obtained by calcination may be pulverized, washed or classified, if necessary. The pulverization may be carried out, for example, using a ball mill or jet mill. The pulverized fluorescent substance B¹ may be heat-treated.

5 Crystallinity of the fluorescent substance B¹ (which is lowered by pulverization) can be enhanced by the heat treatment. The heat treatment may usually be carried out under the same conditions as those for the calcination described above.

Further, the fluorescent substance B¹ used in the present
10 invention may be prepared, for example, by a method described in JP-A-2001-220582.

The phosphor paste according to the present invention is described.

15 The phosphor paste of the present invention includes the above phosphor, a binder and a solvent. A film or a layer can easily be formed on a substrate by coating the phosphor paste on the substrate and heating. The heating is usually carried out at a temperature not lower than a temperature at which the solvent evaporates and lower than a temperature
20 at which the binder decomposes.

The phosphor paste of the present invention may be produced, for example, by a method of mixing the fluorescent substance A¹, the fluorescent substance B¹, a solvent and a binder using an apparatus such as a ball mill, triple roller mill, beads mill and roller mill.

25 Examples of the binder in the phosphor paste include cellulose

resins (ethylcellulose, methylcellulose, nitrocellulose, acetylcellulose, cellulose propionate, hydroxypropylcellulose, butylcellulose, benzylcellulose, modified cellulose and the like), acryl resins (polymers of at least one among monomers including acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, ethyl
5 acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, n-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate,
10 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, benzyl acrylate, benzylmethacrylate, phenoxy acrylate, phenoxymethacrylate, isobornyl acrylate, isobornyl methacrylate, glycidyl methacrylate, styrene, α -methylstyrene, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile and the like), ethylene-vinyl acetate copolymer
15 resins, polyvinyl butyral, polyvinyl alcohol, propylene glycol, urethane resins, melamine resins and phenol resins.

The amount of the binder is usually 5% by weight to 50% by weight based on the total weight of the fluorescent substance A¹ and the fluorescent substance B¹.

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Examples of the solvent in the phosphor paste include monohydric alcohols having a higher boiling point; polyhydric alcohols such as diols and triols typically exemplified by ethylene glycol and glycerin; compounds formable by etherifying or esterifying an alcohol (ethylene
25 glycol monoalkyl ether, ethylene glycol dialkyl ether, ethylene glycol

alkyl ether acetate, diethylene glycol monoalkyl ether acetate, diethylene glycol dialkyl ether, propylene glycol monoalkyl ether, propylene glycol dialkyl ether and propylene glycol alkyl acetate).

The amount of the solvent is usually 100% by weight to 600% by weight based on the total weight of the fluorescent substance A¹ and the fluorescent substance B¹.

Examples

The present invention will be explained in more detail by following examples, which should not be constructed as limiting the invention in any manner.

The brightness of the specimen (phosphor) is measured by the following method:

A specimen is heat-treated in the air at 500°C for 30 minutes and, is exposed to a plasma of 50 W for 15 minutes under an atmosphere of a gas composition: 5% by volume of xenon (Xe) and 95% by volume of neon (Ne) and a pressure: 13.2 Pa.

The obtained specimen was irradiated by vacuum ultraviolet rays using Excimer 146 nm lamp (model H0012, made by Ushio Denki) in a vacuum chamber under pressure of 6.7 Pa (5×10^{-2} Torr) or lower.

Reference 1

The brightness of an aluminate ($\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$, a blue fluorescent substance, average primary particle diameter: 0.4 μm) was measured according to the above method. The brightness of the aluminate

was assumed be 100.

Reference 2

The brightness of a silicate ($\text{Ca}_{0.9215}\text{Sr}_{0.0485}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_6$, a blue
5 fluorescent substance, average primary particle diameter: $1.0\ \mu\text{m}$) was
measured according to the above method. The silicate had a brightness
of 104.

Example 1

10 50 parts by weight of the fluorescent substance in Reference
2 were wet-mixed with 50 parts by weight of the fluorescent substance
in Reference 1 in ethanol to obtain a mixture. The mixture was dried
to obtain a phosphor. The brightness of the phosphor was measured.
The phosphor emitted blue light and had a brightness of 127.

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Example 2

80 parts by weight of the fluorescent substance in Reference
2 were wet-mixed with 20 parts by weight of the fluorescent substance
in Reference 1 in ethanol to obtain a mixture. The mixture was dried
20 to obtain a phosphor. The brightness of the phosphor was measured.
The phosphor emitted blue light and had a brightness of 113.

Example 3

20 parts by weight of the fluorescent substance in Reference
25 2 were wet-mixed with 80 parts by weight of the fluorescent substance

in Reference 1 in ethanol to obtain a mixture. The mixture was dried to obtain a phosphor. The brightness of the phosphor was measured. The phosphor emitted blue light and had a brightness of 107.